

## Chapter 7

# Gasification Technology and Its Contribution to Deal with Global Warming

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**Abstract** It is predictable that energy demand will greatly increase in years to come, due to the continuous growth of world population, together with the quest to improve living standards. CO<sub>2</sub> emissions are hence expected to increase significantly. Gasification is a mature technology for energy production that permits an easier separation of CO<sub>2</sub> for its storage. As modern societies are producing ever-increasing amounts of wastes with negative impact on the environment, new technologies have been developed to co-gasify these wastes either with coal or alone, thus resolving a serious problem of waste disposal. Wastes gasification reduces the dependence on fossil fuels and co-gasification with coal could provide the benefit of security in fuel supply, as the availability of wastes and biomass fuels could vary from region to region and show seasonal changes. Gasification experimental conditions and technologies and syngas cleaning methods are key issues for the production of a clean gas that could find a wide range of applications. This chapter will concentrate on syngas end-uses, focusing on new ones, like gas turbines or engines in IGCC, synthesis of methanol, ethanol and dimethyl ether, Fischer–Tropsch synthesis, and hydrogen production. The role of gasification in CO<sub>2</sub> sequestration will also be discussed.

### 7.1 Introduction

It is predictable that energy demand will have greatly increase in years to come, due to the continuous growth of world population and also because of increasing high quality standards. Energy demand growth, especially from large emerging economies like India and China, may cause substantial alterations in actual world

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organization by raising the price of fossil fuels and by increasing pollutants emissions. To face these challenges and to decrease their impact, it is important to find alternative energy resources. The European Union aims to increase the contribution of renewable energy sources to reach a level of 20% global energy share by 2020 [1]. Most European and USA countries have encouraged the use of renewable energies and the use of biomass and wastes for energy production. On the other hand, fossil fuels will continue to have the greatest share in energy production at least till 2030 with consequent large releases of carbon dioxide ( $\text{CO}_2$ ) emissions, according to IEA predictions [2].

Combustion is the most used technology for energy production, either from fossil fuels or from wastes; however, despite the great efforts to develop new technologies to decrease pollutants emissions from combustion, the release of  $\text{CO}_2$  is still huge and may put life on Earth in danger in the near future. Therefore, the development of new technologies suitable for wastes processing and that may also decrease  $\text{CO}_2$  emissions to prevent global warming is urgent. Gasification may have an important role in achieving these objectives in the near future, as it allows an easier separation of  $\text{CO}_2$  for its sequestration.

Coal gasification is a well known technology but the already available knowledge must be used to research and develop new processes for co-gasification of coal mixed with different types of biomass and wastes with negative impact on the environment. This allows avoiding the serious problems related to waste disposal and the dependence on fossil fuels will be decreased by using alternative fuels.

On the other hand, biomass gasification may also have an important task in attaining European Union objectives for decreasing greenhouse gas emissions, as during biomass growth in a sustainable basis the  $\text{CO}_2$  released during biomass utilization may be mostly absorbed. Despite recent research studies on this subject, cleaning technologies for gasification gas (syngas) are under development and further demonstration of these technologies is still needed.

Nowadays, gasification is deployed all over the world for processing mainly coal and petroleum residuals, like petroleum coke (petcoke). Most installations are in Western Europe, the Pacific Rim, Africa, and North America. Besides the advances of biomass gasification, the success of the gasification process depends on the development of cost-effective and technologically viable gas cleaning technologies, mainly when fuels with considerable amounts of S, Cl, and N are used, which, during gasification, may form several undesirable compounds, some of which may be released into the gas phase. The main gasification drawbacks are related to pollutant emissions, production of inert solid residues, higher product flexibility, and higher efficiency to power, and all of these problems need to be solved. Furthermore, more efficient biomass gasification technologies like Integrated Gasification Combined Cycle (IGCC) need to be fully demonstrated.

Gasification is also a promising process to achieve pre-combustion  $\text{CO}_2$  capture for storage. Coal and/or wastes are first gasified to produce syngas. After syngas cleaning, CO is converted into more  $\text{H}_2$  and  $\text{CO}_2$  in the presence of steam by water-shift reaction. The gas produced contains almost exclusively  $\text{H}_2$  and  $\text{CO}_2$ , whose concentration is much higher than in conventional processes. This feature,

together with the fact that the gas is at high pressure with almost no impurities, facilitates the CO<sub>2</sub> separation process. Pressure swing adsorption, membrane, or cryogenic separation are the most promising technologies to produce a H<sub>2</sub>-rich fuel that can be used in a gas turbine combined cycle or in fuel cells to produce electricity and a CO<sub>2</sub> rich stream ready for storage. Therefore, it is expected that, in the near future, gasification technology may contribute to the production of the energy necessary to ensure economic development and to effective CO<sub>2</sub> sequestration, in order to preserve life on Earth as we know it.

## 7.2 Gasification Fundamentals

Gasification of solid carbonaceous fuels is a very old technology, which has been used on the industrial scale for coal gasification since the seventeenth century. Biomass gasification and pyrolysis was used to produce solid fuel, while the liquid volatiles (tar) had diverse uses like embalming, meat packing, and wood waterproofing in boats in Ancient Egypt and in Greek, Roman, Chinese and other early civilizations both in the Euro-Asian region and in the Americas. During the first half of the twentieth century and up to World War II, several gaseous and liquid fuels were obtained from coal through gasification, especially where petroleum was not available.

Gasification is a thermochemical process that converts carbonaceous materials, usually coal and/or wastes, either used alone or mixed with one another, into a syngas, whose major components are carbon monoxide and dioxide (CO and CO<sub>2</sub>), hydrogen (H<sub>2</sub>), methane (CH<sub>4</sub>), and other gaseous hydrocarbons, usually referred as C<sub>n</sub>H<sub>m</sub>. Gasification commonly uses temperature values higher than 750°C up to 1,300°C, depending on the gasification process used. During carbonaceous materials heating, different processes may occur, namely: (1) *drying* – release of water and of some of the more volatile components at temperature values around 110°C; (2) *devolatilization or pyrolysis* – release of volatile compounds, mainly H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, other gaseous hydrocarbons, NH<sub>3</sub>, H<sub>2</sub>S, and phenols, and formation of char, which is mostly carbon and the mineral matter of carbonaceous materials at temperature values around 350°C; (3) *gasification* – at temperature values higher than 350°C chemical reactions occur between the carbonaceous materials or the char and the chemical species present in the surrounding medium, which include those released during devolatilization and those supplied to the gasification medium, usually air or oxygen, carbon dioxide and/or steam, or a mixture of some of these compounds. Depending on the type of gasification reactor used these processes may occur at different stages, like in fixed bed reactors or almost simultaneously as happens in fluidized beds.

A wide range of chemical reactions may occur during gasification; the more important ones are summarized in Table 7.1.

Air or oxygen added to the gasification medium promotes the oxidation reactions (7.1)–(7.3), supplies the heat necessary for the endothermic reactions, and

releases  $\text{H}_2\text{O}$ ,  $\text{CO}$  and  $\text{CO}_2$  for gasification reactions.  $\text{CO}_2$  may react with solid carbon through the Boudouard reaction (7.4) to release  $\text{CO}$ .  $\text{CO}_2$  may also participate in dry reforming reactions (7.13)–(7.15) to decompose hydrocarbons into  $\text{H}_2$  and  $\text{CO}$ .  $\text{H}_2\text{O}$  may react with solid carbon by water gas endothermic reactions (7.5) and (7.6) to form  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  and may also participate in water gas shift (WGS) reaction (7.8) to convert  $\text{CO}$  into  $\text{H}_2$  and  $\text{CO}_2$ ; this reaction is therefore very important to change syngas  $\text{CO}/\text{H}_2$  ratio.  $\text{H}_2\text{O}$  also takes part in steam reforming reactions (7.9)–(7.12), which convert hydrocarbons into  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ . Hydrocarbons may also be converted by cracking reactions.

On the other hand,  $\text{CH}_4$  may be formed by methanation or hydro-gasification, reaction (7.7) that occurs between carbon and hydrogen. Although it is usually very slow, it may be favored by higher pressure. Hydrogen reforming reaction (7.16) may also form  $\text{CH}_4$ , the reaction between  $\text{H}_2$  and  $\text{CO}$  usually occurring at low temperature, but is favored by higher pressure or in presence of suitable catalysts. As there are many different reactions occurring during gasification, the products of some of them being the reactants of others, it is difficult to understand fully the complex reactions that may occur and thus predict syngas composition.

Syngas heating value depends on the gasification medium used. Though the use of air has the advantage of supplying the heat necessary for gasification endothermic reactions, the syngas produced has a low heating value, usually  $3.5\text{--}7\text{ MJ/m}^3$ , due to nitrogen diluting effect. The use of oxygen, instead of air, allows overtaking the diluting effect of nitrogen, thus syngas has a higher heating value, usually  $9\text{--}15\text{ MJ/m}^3$ , but due to the oxygen production cost, operating costs are higher. Other gasification systems use only steam as gasification medium, which also overtakes the diluting effect of nitrogen and, though steam production is cheaper

**Table 7.1** Most important gasification reactions

Designation	Mechanism	$\Delta H$ (kJ/mol)
Oxidation	$\text{C}_{(\text{s})} + \text{O}_2 \rightleftharpoons \text{CO}_2$	-392.5 (7.1)
	$\text{C}_{(\text{s})} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}$	-110.5 (7.2)
	$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	-242.0 (7.3)
Boudouard	$\text{C}_{(\text{s})} + \text{CO}_2 \rightleftharpoons 2\text{CO}$	172.0 (7.4)
Water Gas: primary	$\text{C}_{(\text{s})} + \text{H}_2\text{O} \rightleftharpoons \text{CO} + \text{H}_2$	131.4 (7.5)
	secondary $\text{C}_{(\text{s})} + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 2\text{H}_2$	90.4 (7.6)
Methanation	$\text{C}_{(\text{s})} + 2\text{H}_2 \rightleftharpoons \text{CH}_4$	-74.6 (7.7)
Water-gas shift	$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$	-41.0 (7.8)
	$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	205.9 (7.9)
	$\text{CH}_4 + 2\text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 4\text{H}_2$	164.7 (7.10)
Steam reforming	$\text{C}_n\text{H}_m + n\text{H}_2\text{O} \rightleftharpoons n\text{CO} + (n + m/2)\text{H}_2$	210.1 (7.11)
	$\text{C}_n\text{H}_m + n/2\text{H}_2\text{O} \rightleftharpoons n/2\text{CO} + (m - n)\text{H}_2 + n/2\text{CH}_4$	4.2 (7.12)
	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247.0 (7.13)
$\text{CO}_2$ reforming	$\text{C}_n\text{H}_m + n\text{CO}_2 \rightleftharpoons 2n\text{CO} + m/2\text{H}_2$	292.4 (7.14)
	$\text{C}_n\text{H}_m + n/4\text{CO}_2 \rightleftharpoons n/2\text{CO} + (m - 3n/2)\text{H}_2 + (3n/4)\text{CH}_4$	45.3 (7.15)
$\text{H}_2$ reforming	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	-205.9 (7.16)

than oxygen, the heat necessary for gasification process needs to be supplied by external media, either by an inert material like sand (Battelle process) or by a hot fluid circulating through a heat exchanger placed inside the gasifier. Both processes also increase gasifier operating costs.

The production of syngas through gasification is always associated with the release of tar. Tar is a complex mixture of high molecular weight hydrocarbons that may contain different compounds from single ring to five-ring aromatic compounds together with other hydrocarbons containing oxygen and complex polycyclic aromatic hydrocarbon (PAH). The presence of tar may cause several problems, namely sticky deposits that may cause blocking of pipes, gas coolers, filter elements, engine suction elements and tar may also deposit on catalyst surface, deactivating the catalyst that may be used in a downstream process, like: steam reforming, water gas shift reaction, and chemical synthesis. Tar deposition in gas turbines, engines, or boilers causes severe mechanical damage, and therefore most syngas end-uses require very low tar contents, as shown in Table 7.2. Tar abatement is a key issue in gasification and syngas cleaning processes. Several authors have been developing different types of catalysts with the aim of getting a catalyst with high performance and low cost. The catalysts used so far may be divided into four groups: (1) natural minerals (limestone, dolomite, olivine), (2) alkali metals ( $\text{KOH}$ ,  $\text{KHCO}_3$ , and  $\text{K}_2\text{CO}_3$ ), (3) Ni-based and (4) noble metal catalysts (Rh, Ru, Pt, and Pd). Some of these catalysts have been tested inside the gasifier by Pinto *et al.* [3] and/or in a secondary reactor for syngas cleaning, leading the second option for higher tar abatement by Pinto *et al.* [4]. Further research and development is still required till more effective catalysts for tar abatement are found, the main challenges being the development of catalysts with longer lifetimes, higher mechanical strength, low cost, and high tar decomposition capacity.

Besides the mentioned syngas components, other undesirable compounds may also be formed, especially when low grade coals or wastes are gasified. When carbonaceous materials with high contents of N, S, and halogens are gasified, the formation of  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  is expected, due to the reducing gasification conditions. These compounds are pollutant precursors as they originate  $\text{NO}_x$  and  $\text{SO}_x$  when syngas is burned for energy production. On the other hand,  $\text{H}_2\text{S}$  may also poison catalysts used in syngas cleaning processes.

The formation of  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  may be controlled through the adjustment of gasification operating parameters, such as size, shape, structure and mineral composition of carbonaceous materials, gasification medium, temperature and heating rate, and the use of specific catalysts or sorbents by Pinto *et al.* [5]. These parameters also affect gasification performance and syngas properties and composition.

Usually syngas produced by gasification does not have the suitable characteristics required by its utilizations so gas conditioning is necessary to decrease to low levels the contents of undesirable compounds such as tar,  $\text{H}_2\text{S}$ ,  $\text{HCl}$ , and  $\text{NH}_3$ . The presence of these compounds increases operational costs, since they poison and deactivate catalysts, but also promote and increase corrosion in the equipment. On the other hand, as they are pollutant precursors, the presence of such contaminants is environmentally adverse and must comply with emission limits legislation.

Therefore, the reduction of these compounds' contents is fundamental. When the syngas is going to be used at atmospheric and temperature conditions a possible option for syngas conditioning is wet scrubbing. However, if the syngas is going to be used in any thermal process, such as shift reactor or chemical synthesis, hot gas cleaning processes are the best option, as they allow higher energy efficiency and avoid the production of wastewater contaminated with tar, inorganic acids,  $\text{NH}_3$ , and metals.

To sum up, it may be said that the most efficient way to remove tar,  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$  is by several steps, beginning with a cheaper material that removes the larger fraction of  $\text{H}_2\text{S}$  and  $\text{HCl}$ , being followed by a more specific catalyst that may remove the remaining tar. Pinto *et al.* [4] tested a configuration with two catalytic fixed bed reactors, the first one with dolomite to retain  $\text{H}_2\text{S}$  and  $\text{HCl}$  and to promote some tar decomposition and the second one with a more expensive Ni-based catalyst to eliminate completely tar and gaseous hydrocarbons, apart from methane. This configuration proved to be suitable to treat syngas with high contents of tar, sulfur and halogen compounds, which by being retained in dolomite reactors will ensure a longer life for Ni-based materials used in the second reactor. This configuration could be simplified by suppressing the dolomite reactor whenever the syngas has low  $\text{H}_2\text{S}$  and  $\text{HCl}$  contents or by omitting the Ni-based catalyst reactor when either the syngas has low tar contents or its application is not very exigent towards the existence of tar.

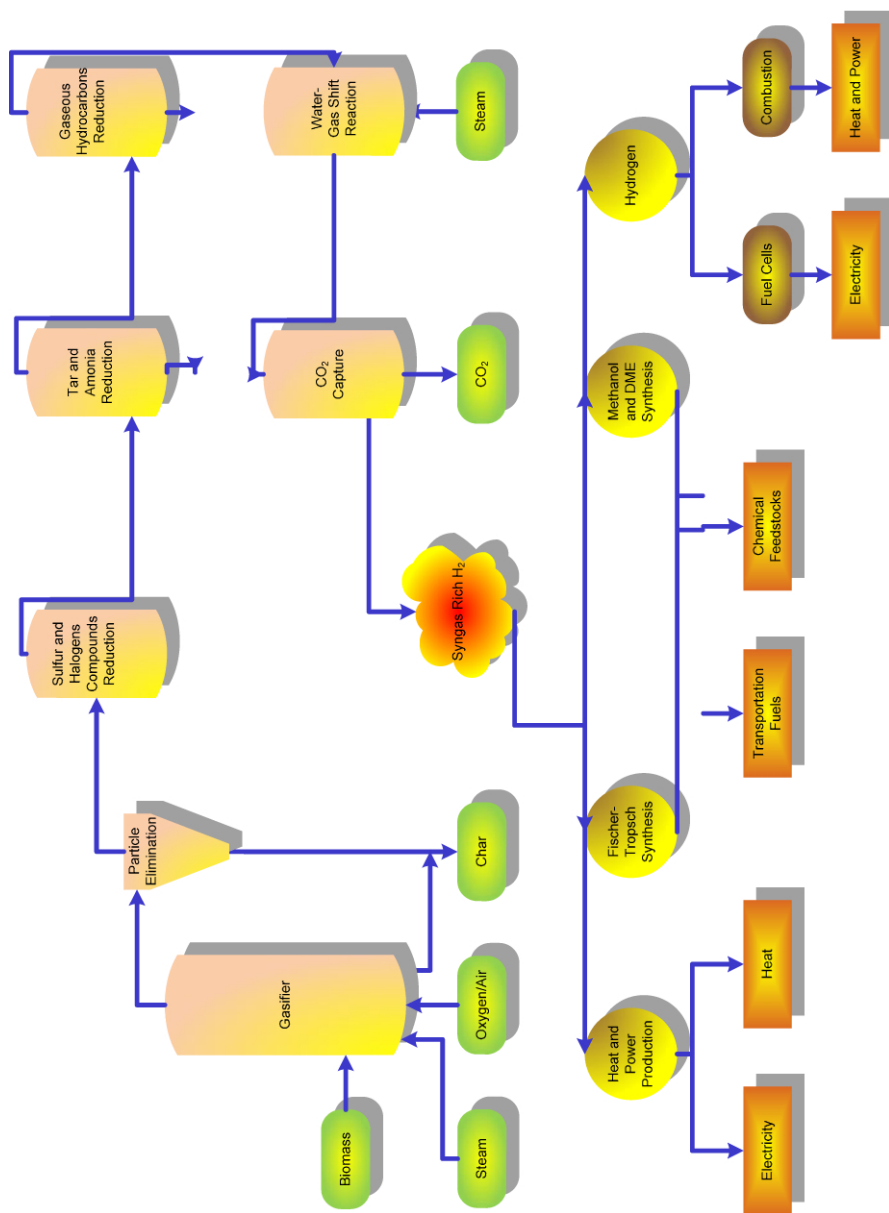
## 7.3 Syngas Utilizations

### 7.3.1 Introduction

Syngas may have a large range of end-uses. However, most of them are very demanding towards syngas quality and impurities contents, as summarized in Table 7.2, which obliges a more or less complex syngas cleaning process, depending on syngas composition. In Figure 7.1 one possible configuration is presented for hot syngas conditioning, which may be simplified depending on the type and composition of carbonaceous materials gasified, gasification conditions, and addition of catalysts or sorbents. In Figure 7.1 there are also presented syngas applications in different conversion processes and the main product obtained in each one.

Nowadays, the production of heat and power has two main challenges: the increase of processes efficiency and the minimization of green house gas emissions. Due to the large reserves of coal and to the possibility of using it mixed with wastes, the use of syngas for heat and power production has grown in importance and interest. Syngas may be used in boilers or combustors for heat production, which are less demanding towards syngas quality and characteristics than some other syngas utilizations like motors or turbines, since the presence of small amounts of tar and other impurities are allowed in syngas, as shown in Table 7.2.

Usually the flue gas produced by an IGCC system is fed to a gas turbine, fuel cell, and steam turbine for power generation, and a steam generator for heat recovery. In a gas turbine, due to the formation of alkali sulfates, the  $\text{H}_2\text{S}$  concentration must be limited to less than 20 ppm to protect it from high temperature corrosion.



**Figure 7.1** Possible configuration for hot syngas conditioning and syngas main applications

**Table 7.2** Syngas characteristics and quality demanded by different utilizations

Impurity	Boiler	Gas engines	Gas turbines	Fuel cells	Chemical synthesis
Particulate (mg/Nm <sup>3</sup> )	1,000	< 50	< 15	< 0.1	Almost completely removed
Particle size (μm)	10	< 10	< 5	< 10	
Tar (Dew point)	< 400°C	< 10°C		–	Not condensing below dew point
Alkali metals		0.24 mg/Nm <sup>3</sup>	0.24 mg/Nm <sup>3</sup>	< 10 ppm	10 ppbv
NH <sub>3</sub>	–	< 50 mg/Nm <sup>3</sup>		< 5000 ppm	1 ppmv
Total sulfur	72 mg/Nm <sup>3</sup>	< 80 mg/Nm <sup>3</sup>		< 1 ppm	< 1 ppmv
Total chlorine	35 mg/Nm <sup>3</sup>	< 100 mg/Nm <sup>3</sup>		< 1 ppm	10 ppbv

The Ni catalyst and anode of the fuel cells are poisoned by H<sub>2</sub>S, resulting in loss of cell voltage; therefore its concentration must be reduced to under 1 ppm as reported by Ohtsuka *et al.* [6].

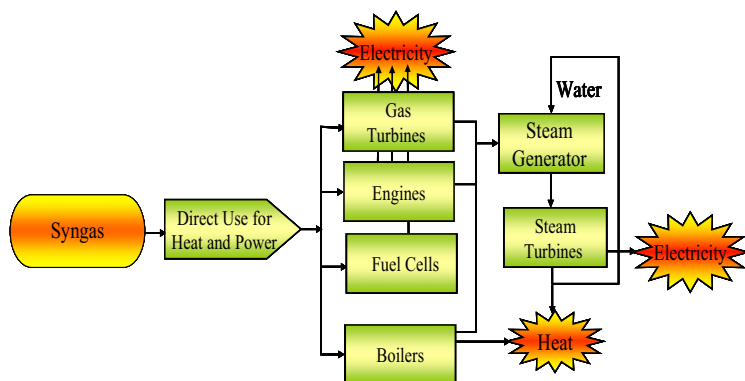
Due to the low heating value of syngas produced when air is used as gasification medium (3.5 MJ/m<sup>3</sup> and 7 MJ/m<sup>3</sup>), syngas transport and storage is not economical viable. Therefore, syngas should be burned near the gasifier to decrease heat losses and to guarantee a high global efficiency. When gasification takes place in the absence of air, syngas has a medium heating value, usually 9–15 MJ/m<sup>3</sup>, which allows its transportation, storage, and utilization in different applications.

### 7.3.2 Heat and Power Production Through Engines and Turbines

When the syngas has low contents of particulates and tar it can be used in gas turbines or in motors as far as it fits the requirements of Table 7.2. In gas turbines, syngas chemical energy is converted into mechanical energy, which is used to produce electricity. In engines syngas is burned and converted into CO<sub>2</sub> and H<sub>2</sub>O. Syngas has been used in engines, though, as reported by Sridhar *et al.* [7], the combustion chamber should be modified in relation to that used for diesel, to decrease energy losses and increase efficiency.

The remaining heat of the exhaust gas that leaves the turbine, the engine, or the boiler may be used to produce steam which, when used in a steam turbine to produce additional electricity, allows increasing of the energy conversion efficiency of the overall process, as shown in Figure 7.2. This concept is used in IGCC, which are great energy management installations and may be considered to be a relatively environmentally friendly method of using coal, especially when they also integrate CCS (carbon capture and sequestration) units to decrease CO<sub>2</sub> emissions. IGCC installations may present different configurations, incorporating gasification units with gas cleaning processes and power production units with engines and/or gas and steam turbines. There are commercial and demonstration



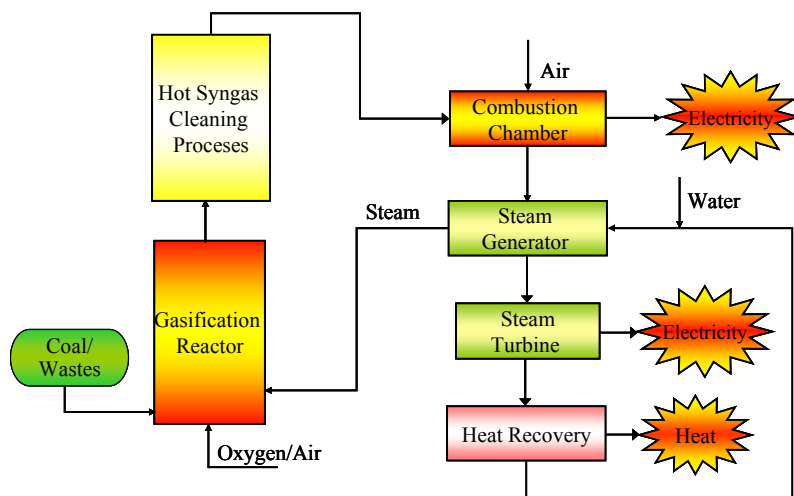


**Figure 7.2** Direct use of syngas for heat and power production

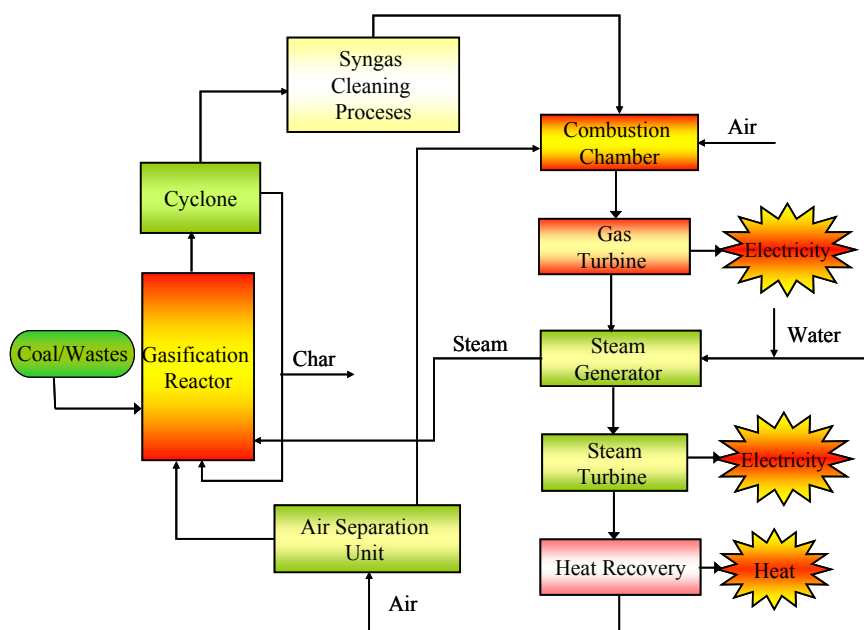
IGCC installations for power generation from natural gas or from syngas produced by coal gasification in the United States, Europe and Japan.

In Figures 7.3 and 7.4 are presented general configurations for IGCC installations using engines or turbines, respectively. In Figure 7.4 is also considered an air separation unit to produce oxygen for the gasifier, using the nitrogen stream to introduce inside the combustor, because Frey *et al.* [8] analyzed different integration possibilities by simulation using ASPEN Plus with and without air extraction and nitrogen injection and combinations of both at different pressures and concluded that nitrogen injection at elevated pressure led to high efficiency and to low emissions.

Mondol *et al.* [9] used the software ECLIPSE to evaluate the techno-economic performance of four new concepts for IGCC with CO<sub>2</sub> capture facilities, which



**Figure 7.3** Schematic diagram for general configuration of IGCC installation, combining the gasifier and syngas cleaning systems with an internal combustion engine



**Figure 7.4** Schematic diagram for general configuration of IGCC installation, integrating the gasifier and syngas cleaning units with gas and steam turbines

were compared with two conventional IGCC with and without CO<sub>2</sub> capture. In the new IGCC concepts different options were considered, for instance, air-blown regenerator or oxygen-blown, cryogenic air separation unit for O<sub>2</sub> supply, or membrane separation, for flue gas treatment were also considered different choices, triple-pressure or single-pressure drum-type heat recovery steam generator for heat recovery or amine scrubber, *etc.* According to the authors, the new IGCC plants with CO<sub>2</sub> capture have efficiencies 18.5–21% higher than that of the conventional IGCC CO<sub>2</sub> capture plant. The CO<sub>2</sub> capture efficiencies of the new concepts were 95.8–97%, against 87.7% of the conventional plant. The investments costs for the proposed new plants varied in the range 1207–1479 €/kW<sub>e</sub>, depending on the concept considered, while the investments costs of the conventional plants were 1620 €/kW<sub>e</sub> or 1134 €/kW<sub>e</sub>, respectively, for plants with and without CO<sub>2</sub> capture. Therefore, Mondol *et al.* [9] concluded that the new plants were more efficient, cleaner, and produce electricity at a cheaper price than the conventional ones.

IGCC energy conversion efficiency is usually around 40–45%, but several authors have studied different configurations with the aim of increasing these figures, using specific or dedicated software, such as: ASPEN or ECLIPSE. Some of these new concepts also include CCS installations.

Brown *et al.* [10] studied the thermo-economic aspects of the conversion of biomass into energy. Different options were studied for fluidized bed gasifier operation: atmospheric or pressurized air, oxygen, or steam. The gasifier was

connected to an internal combustion engine combined cycle ICE-CC or to gas turbine combined cycle (GT-CC). The ICE-CC required a cold gas cleaning system with tar concentrations below  $100 \text{ mg/Nm}^3$  and particulates lower than  $50 \text{ mg/Nm}^3$ , while GT-CC demanded tar concentrations and particulates minor than  $5 \text{ mg/Nm}^3$  and  $30 \text{ mg/Nm}^3$ , respectively. According to the authors' simulation results, electricity conversion efficiencies were higher for ICE-CC, while GT-CC led to lower investment costs and to optimal capital costs and electricity generation costs. The best specific capital costs were calculated for steam gasification, followed by air gasification and then for oxygen gasification, always for GT-CC. In relation to annual electricity generation costs the differences among different oxidants were narrow; however, air gasification was optimal for GT-CC and steam gasification for ICE-CC. According to the authors, the models used still need some improvement, for instance the reaction model needs further calibration to take into account product formation at different pressures and in presence of other oxidants than air.

Chen *et al.* [11] also studied the implications of adding a CCS unit to an IGCC plant. The studied system integrated a quench gasifier with water gas shift reactor and a Selexol system to remove sulfur and  $\text{CO}_2$ . These authors analyzed the effect of different parameters on plant performance and cost, such as cost and quality of coal gasified and  $\text{CO}_2$  removal efficiency. As coal quality increased, gasification efficiency, thermal efficiency and capital cost of power plant also increased. The cost of removing  $\text{CO}_2$  decreased with the rise of  $\text{CO}_2$  removal efficiency, being 90% the optimal value. When advanced technologies for oxygen production and for gas turbines were considered the efficiency increased and the cost of IGCC systems decreased both with and without CCS. The joining of advanced technologies with CCS led to an increase in capital cost, but due to the higher efficiency the estimation for the cost of electricity was lower than that of current plant.

Many other authors have studied different configurations for IGCC (Lee JJ *et al.* [12], Wu C *et al.* [13], Christou *et al.* [14], Sudiro *et al.* [15], and Franco *et al.* [16]). Some of them integrated advanced technologies on which there is not enough information and data, and therefore some of these studies present significant uncertainties in relation to efficiency and cost estimations.

### 7.3.3 Hydrogen Production

The growing interest in hydrogen utilization is mainly due to environmental concerns and the security of fossil fuels supplies. The main advantage of using hydrogen as an energy carrier is the environmental benefits over fossil fuels. However, currently, hydrogen is mainly produced through fossil fuels. In the near future it is expected to be able to produce hydrogen from biomass gasification in a clean and efficient way. Nevertheless, there are some technical problems that need to be solved before biomass gasification may become a feasible way of producing hydrogen. One of the challenges is to increase hydrogen content in syngas through

WGS reaction (7.8). The conversion of CO with steam to produce  $H_2$  is usually improved by moderate temperature, by removing the hydrogen to shift the WGS equilibrium to the right, or by using excess steam and suitable catalysts.

The removal of CO from the syngas is crucial if the objective is to use the hydrogen in fuel cells, as this compound is poisonous for this kind of application. The main challenge in this field is the development of suitable catalysts for this reaction, in order to make the hydrogen production from biomass gasification economically and technically more attractive.

Extensive research on WGS catalysts has been reported in the literature. There are two main groups of catalysts to be used in WGS reaction: those applied at higher temperature (320–450°C) and others operating at lower temperatures (200–250°C). In the first group, iron-chromium based catalysts are mainly used and in the second copper-zinc based catalysts. The Fe–Cr formulation was reported in 1912 and since then studies with different promoters such as B, Cu, Ba, Pb, Hg, Ag, B, Ce, Zn, and Co have been reported by Zhang *et al.* [17]. Other metals such as Sn, Ce, Ru, and Rd (Basinska *et al.* [18]) and zeolites (Souza *et al.* [19]) have also been tested to increase the WGS reaction performance. Apart from this, gold based catalysts and platinum group metals have been proved to facilitate the WGS reaction, as reported by several authors, including Yeung and Tsang [20] and Andreeva *et al.* [21].

After the WGS reaction, the separation of  $CO_2$  from the gases is needed to obtain high purity hydrogen. There are four major possible ways of accomplish this separation: chemical or physical absorption, pressure swing adsorption (PSA), cryogenic separation, and membrane separation. For a preliminary choice of the separation technology one should take into account the operating temperature and pressure ranges to be used, the syngas composition ( $CO_2$ , concentration and nature of other components present in the feed stream), and process cost. All of these technologies have limitations: PSA works at room temperature and high pressure and recovers less of the feed-stream hydrogen; cryogenics separation is normally used only in large-scale facilities, because it has a high capital cost; current polymer membrane separation systems have limited temperature tolerance and are also more vulnerable to chemical damage from aromatics compounds and  $H_2S$ .

$CO_2$  can be separated from  $H_2$  by chemical or physical absorption using liquid solvents. The main disadvantage of the absorption process is that, in all cases, the solvent recycling is energy and capital demanding. Solvents frequently used in chemical absorption are alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), di-isopropanolamine (DIPA), methyldiethanolamine (MDEA), and diglycolamine (DGA) (McKee [22], Ebner and Ritter [23]). Ammonia and alkaline salt solutions are also used. Before  $CO_2$  removal, the syngas has to be cooled and cleaned to remove particulates and other impurities. Then the clean gas passes through an absorption tower, where the absorption solution is placed. The separation occurs by a selective absorption of  $CO_2$  by the solvent, which reacts chemically with  $CO_2$  producing a weakly bound compound. After the absorption step,  $CO_2$  is released in a stripper tower by reducing the pressure or raising the temperature to approximately 120°C.

In the physical absorption process the solvent only interacts physically with the dissolved gas and the relative absorption of  $\text{CO}_2$  in solvent is favored over other components of the gas mixture. The most common physical solvents used are organic compounds with low surface tension, such as: methanol (Rectisol Process) and glycol ethers (Selexol Process), propylene carbonate (Fluor solvent process), and sulfolane. Also calcium oxide ( $\text{CaO}$ ), sodium hydroxide ( $\text{NaOH}$ ), and potassium hydroxide ( $\text{KOH}$ ) are used as absorption solvents. This process can be used in various applications, but is considered the best choice for applications at higher pressure (*i.e.*, IGCC). The most used adsorbents include aluminosilicate zeolite molecular sieves, titanosilicate molecular sieves, and activated carbons (Ebner and Ritter [23]).

The PSA process is, currently, the most used. Other adsorption techniques for  $\text{CO}_2$  capture have been developed, *e.g.*, temperature swing adsorption (TSA) and electrical swing adsorption (ESA); however they are not so popular (McKee [22]). A typical PSA unit consists of a series of containers, each holding the same type of adsorbing material. The PSA separation technology is a cycling process with two basic steps, the gas compound adsorption and the adsorption material regeneration. The utilization of at least two adsorbent vessels allows an almost continuous process of obtaining hydrogen. The gases are separated according to the characteristics of the molecular species and affinity for a specific adsorbent material (*e.g.*, zeolites and activated carbon). After the process is completed it swings to low pressure to desorb the adsorbent material. The adsorption material regeneration takes place after the adsorption bed reaches the end of its capacity to adsorb  $\text{CO}_2$ , then the feed gas is switched to a second adsorption bed, and the first one is regenerated by depressurizing the adsorbent bed. It is then ready for another cycle of producing high purity hydrogen. Also, the off going gas of the vessel being depressurized can be used to pressurize partially the second vessel. This procedure has the advantage of saving a significant amount of energy, so it is commonly used on an industrial scale. The  $\text{CO}_2$  obtained after regeneration shall be compressed for transport and storage. The parameters that were shown to have more effect on the adsorption efficiency are temperature, partial pressures, surface forces, and adsorbent pore sizes. The two main advantage of PSA process is high purity hydrogen production (up to 99.999 vol.%) and the ability of removing CO and  $\text{CO}_2$  to very low concentrations (0.1–10 ppmv).

The TSA process is very similar to PSA, the main difference being that the adsorbent regeneration occurs by raising the temperature. The ESA process uses as adsorbent a carbon-bonded activated carbon fiber. Adsorbent efficiency to adsorb  $\text{CO}_2$  can vary depending on the pore volume and size and surface. This is a new material that is highly conductive, so the desorption of the adsorbed gases occurs rapidly by low-voltage electrical current with no variation in the system pressure and with a very small modification on the system temperature.

Cryogenic separation uses gas condensation as the separation principle. The  $\text{CO}_2$  is physically separated from  $\text{H}_2$  by condensation at cryogenic temperatures. The phase modification (gas to liquid or solid) is induced by compressing and cooling the gas mixture in a multiple stage process, which is more efficient if the

gas mixture contains compounds with significant differences in boiling points (Shackley and Gough [24]). Usually this process is only used for gas mixtures with very high CO<sub>2</sub> yields, usually higher than 90% (Shackley and Gough [24]). The presence of impurities (SO<sub>2</sub> and NO<sub>x</sub>) can complicate the separation, so a previous gas cleaning is essential. Furthermore, the gas has to be dried before being cooled down, because the presence of water complicates the process. The main disadvantage of the cryogenic separation is the high energy needed for gas cooling and pressurization that make this process very expensive. An advantage of this process is that the liquid CO<sub>2</sub> is easier to transport since it does not need compression.

Membrane technology is considered as an attractive way of separating CO<sub>2</sub> from gas streams. A membrane is a selective barrier between two phases, in which some components pass through it while others are retained. The highest developments in membrane technology occurred during the 1980s, due to the development of synthetic polymeric membranes (Basu *et al.* [25]). Currently, commercially membranes of a wide range of materials are available, metallic, ceramic or organic. Nowadays, membranes are still too expensive and energy demanding to be implemented on a large scale.

The high processing costs associated with the absorbent/adsorbent regeneration and phase exchange (gas to liquid) are eliminated in membrane separation processes, which present certain advantages over other separation methods, namely low maintenance, low energy requirements, and being environmental friendly (Basu *et al.* [25]). Other advantages include compactness, light weight, and modular design, allowing a multi-stage operation.

For a membrane to be suitable for H<sub>2</sub> removal it needs to have a high selectivity for H<sub>2</sub> and high permeability. The high permeability is necessary to produce a compact membrane facility, since many current systems require a large membrane area to achieve the desired gas stream purity and flow rate. So, new membrane types are essential to attain high permeability and selectivity, as well as long-term durability.

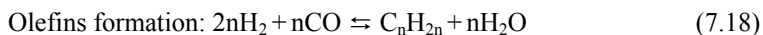
### 7.3.4 Fischer–Tropsch Synthesis

The process by which CO undergoes hydrogenation over iron, cobalt, or nickel catalysts at atmospheric pressure and temperatures of 180–250°C, leading to a mixture of linear and branched hydrocarbons and oxygenated products, is named the Fischer–Tropsch synthesis (FTS). The FTS provides alternative routes for the production of transportation fuels and petrochemical feedstock. This process can be designed to produce gasoline, diesel, and/or chemicals. In 2002 two Fischer–Tropsch synthesis (FTS) plants existed as commercial operations, *i.e.*, Sasol in South Africa and Shell in Malaysia, but interest in the FTS technology has increased due to decreasing oil reserves, the geographic location of these reserves, the demand for cleaner feedstock, and the reduction of CO<sub>2</sub> emissions. In 2005 the

American company Rentech explored four pilot installations and a semi-commercial facility for FTS. The companies Sinopec and Syntroleum announced their intention to start building, in 2007, two installations, one in China and the other in Papua New Guinea (Boerrigter [26]).

The FTS has been specially used with syntheses gas produced from coal gasification (Boerrigter [27]). More recently, the interest in using this technology combined with biomass gasification has increased dramatically, due to the decision of the European Commission to substitute 20% of conventional fuels by alternative fuels in the road transport sector by the year 2020 (EU [28]). The combination of biomass gasification with FTS is designated as biomass-to-liquids (BTL). Nowadays, the main objective of the research and development projects are the production of second generation bio-fuels by biomass and/or wastes gasification combined with FTS.

Syngas produced by gasification process needs to be cleaned and conditioned to meet the required specifications to be used in FTS, as mentioned in Table 7.2. The extensive cleaning is needed because the catalyst lifetime is greatly affected by the presence of trace pollutants, which can lead to changes in the physical and chemical properties of the catalysts. Conditioning is needed to adjust the  $H_2/CO$  ratio to approximately 2, due to the stoichiometry of the FTS reactions. This adjustment is performed by water gas shift reaction (7.8), followed by a  $CO_2$  removal unit. In FTS  $CO$  reacts with  $H_2$  to produce mainly linear paraffins and  $\alpha$ -olefins by reactions (7.17) and (7.18), which are highly exothermic reactions:



The most frequent FTS catalysts used have metals from groups 8, 9, and 10 (formerly group VIII) like Fe, Co, and Ru. The iron based catalysts are the most used in FTS due to their lower cost in comparison with other active metals. They are normally used in FTS using syngas from coal (Wu *et al.* [13]) but are promising option for biomass conversion (Steen and Claeys [29]). To obtain highly active FTS catalysts, the promotion of the iron based catalyst is required (Steen and Claeys [29]). Several promoters have been tested, but the potassium appears to be the most cost effective promoter (Luo and Davis [30]). A lot of work has been done to develop new and more efficient iron catalysts (Wu *et al.* [13]).

Cobalt based catalysts present the highest activity and generate predominantly linear alkanes. Also, these catalysts are not inhibited by water, resulting in a higher productivity and high synthesis gas conversion (Borg *et al.* [31]). The main disadvantages of these catalysts are the low water gas shift activity and high cost of cobalt. Inorganic supports with high surface area (*e.g.*, silica, alumina) have been studied to increase the surface area of these catalysts (Borg *et al.* [31], Bao *et al.* [32], Song and Li [33], Storsæter *et al.* [34]), but alumina appears to be the best choice (Steen and Claeys [29]). The use of various support materials such as  $SiO_2$ ,  $Al_2O_3$ , and  $TiO_2$  have been patented.

Ruthenium based catalysts are the most active for FTS, but the high price of ruthenium eliminate its application on the industrial scale. At low operation temperatures and high pressures the Ruthenium based catalysts are selective towards high molecular waxes, but at relatively low pressures produce a large amount of methane.

Many comparative studies of different catalysts for FTS have been published, but the catalytic activity of each of these catalysts with respect to the FTS reaction is still controversial. Also, the particle size and dispersion of the catalyst has an important role in its selectivity and activity. The conversion of gas to hydrocarbons (Gas-To-Liquids route) is currently one of the most promising topics in the energy industry due to economic utilization of wastes to produce environmentally clean fuels, which can have many applications. The FTS technology allows the utilization of biomass and wastes as feedstock in the fuels market.

### 7.3.5 *Synthesis of Methanol and Dimethyl Ether*

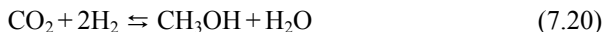
The methanol and dimethyl ether (DME) syntheses have attracted great interest because of their potential to be used as fuels and as chemicals. Methanol can be used directly or blended with other petroleum products as a clean burning transportation fuel and is also an important chemical intermediate used to produce a large number of chemicals.

The most widely used feedstock for methanol and DME production is natural gas, but other feedstocks can be employed. Coal is increasingly being used in methanol production, via gasification and syngas production, especially in China. Moreover, well established technologies already available are being applied for methanol production using the syngas obtained during biomass gasification, due to the possibility of energy production and greenhouse gas emissions reduction. Many studies were performed in methanol synthesis from biomass-derived syngas (Kumabe *et al.* [35], Zhang *et al.* [17]). Several biomass-to-methanol demonstration projects have been developed, such as the Hynol project in the United States, the BAL-Fuels (Biomass-Derived Alcohols Fuels), BioMeet, and BLGMF projects in Sweden, and the BGMSS project in Japan (Zhang *et al.* [17]).

The Syngas produced needs to be extensively cleaned and conditioned before it may be used for methanol or DME synthesis, the required specifications being similar to those for FT synthesis (Table 7.2). Also, a syngas with  $H_2/CO$  ratio of approximately 2 is needed, so a WGS reaction is required. Syngas produced during biomass gasification has a different composition from that derived from natural gas or coal. It contains higher amounts of  $CO_2$  and lower amounts of  $H_2$ , which results in a low H/C ratio and a high  $CO_2/CO$  ratio (Yin and Leung [36]). This higher percentage of  $CO_2$  led to the idea of using  $CO_2$ , the most important greenhouse gas, as an alternative feedstock, replacing CO in the methanol production. In the methanol synthesis CO and  $H_2$  react to produce methanol by reaction (7.19). Methanol can also be produced by  $CO_2$  hydrogenation, according to reac-



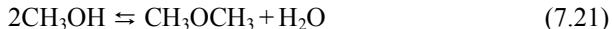
tion (7.20). The carbon source for methanol synthesis is still under debate (Liu *et al.* [37]):



The main challenge of methanol and DME synthesis is the development of more efficient catalysts. Several research groups have been working in catalyst preparation using different catalyst compositions and preparation methods; however, uncertainties still remain about the role of active catalyst sites, the effect of various promoters addition, and reaction mechanism. Recently, new catalysts based on nickel, copper, zinc and alloys, and also ultrafine particle catalysts have been proposed for methanol synthesis (Venugopal *et al.* [38], Kiss *et al.* [39]).

The properties of catalysts used in methanol synthesis have been extensively studied, but Cu still continues to be an important active catalyst component (Liu *et al.* [37]). Also, some studies on catalysts for methanol synthesis from  $\text{CO}_2$  hydrogenation have been performed (Liu *et al.* [37], Liang *et al.* [40]). These studies showed that the Cu/ZnO-based catalysts modified with different metals or oxides exhibit considerable activity and selectivity for the methanol production via  $\text{CO}_2$  hydrogenation (Melián-Cabrera *et al.* [41], Liu *et al.* [37], Liang *et al.* [40]).

The DME synthesis consists of two steps: the methanol synthesis followed by methanol dehydration by reaction (7.21):



The research studies have been focused on the development of better catalysts with higher selectivity for DME formation. Some research groups tried to find bifunctional catalysts (Ge *et al.* [27]). These catalysts present two types of active sites: one for methanol synthesis and the other for methanol dehydration (Ge *et al.* [27]). Others have reported that the catalysts more suitable for DME synthesis were mostly Cu/ZnO based catalysts (methanol synthesis catalyst) mixed with a solid acid catalyst, such as  $\gamma$ -alumina or zeolites (methanol dehydration catalysts) (Yaripour *et al.* [42], Venugopal *et al.* [38]).

The key issue to chemical synthesis from syngas is the development of more efficient and lower cost catalysts. Many studies have been performed, but there are still a lot of improvements to be achieved.

## 7.4 The Role of Gasification in CCS and in Global Warming Abatement

Many countries compromised to decrease greenhouse gas emissions since the Kyoto protocol. To achieve this goal several strategies may be followed, increasing electricity and power generation efficiency, raising the role of bio-wastes for

energy production, and increasing the share of renewable and nuclear sources for energy production. However, nuclear energy is not well accepted by common citizens and most renewable technologies are not yet sufficiently advanced to allow fossil fuels substitution. Therefore, according to current predictions, fossil fuels like coal, oil, and natural gas will continue to have the greatest contribution for energy production, at least till 2030, around 85% of today's needs, IEA [2]. Consequently, it is of great importance to develop new technologies for energy production from fossil fuels that could diminish CO<sub>2</sub> emissions, facilitate CO<sub>2</sub> capture and storage, and increase energy efficiency.

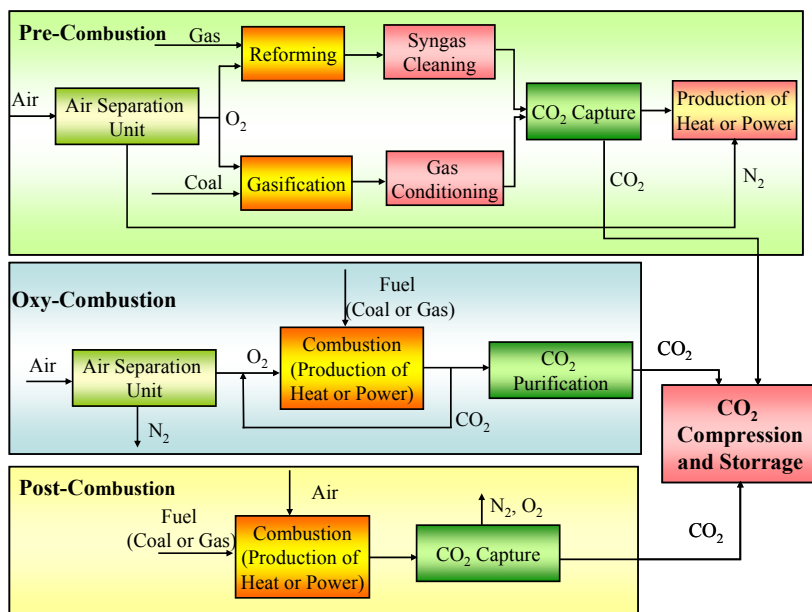
The use of coal for electricity production will continue to be significant and technologies for clean coal are most needed. Different options may be considered for CO<sub>2</sub> capture, as shown in Figure 7.5:

- pre-combustion, (production of syngas by gasification or pyrolysis processes, conversion of CO into CO<sub>2</sub>, and CO<sub>2</sub> capture);
- oxy-combustion (combustion with pure O<sub>2</sub> with recycled flue gas and purification of CO<sub>2</sub> to remove impurities and incompressible gases);
- post-combustion (air combustion and removal of CO<sub>2</sub> from exhaust gases).

In coal combustion systems with air, CO<sub>2</sub> is emitted in large quantities and its sequestration is not very attractive, because CO<sub>2</sub> is diluted in N<sub>2</sub> and large amounts of flue gases need to be treated for N<sub>2</sub> separation from CO<sub>2</sub>, prior to CO<sub>2</sub> sequestration by expensive processes. In fact, CO<sub>2</sub> adsorption, membranes, and cryogenic separation are not suitable. Cryogenic separation needs much energy, due to the low content of CO<sub>2</sub> in the exhaust gases and is too expensive, especially for gases at atmospheric pressure. Membranes are not suitable due to the existence of dust, SO<sub>x</sub>, NO<sub>x</sub> and incompressible gases, and due to membranes physical degradation. CO<sub>2</sub> adsorption on a solid is also not adequate because of exhaust gases high flows and impurities. Chemical absorption technologies are probably the most adequate. However, the choice of the method depends on exhaust gas characteristics and, though different amines have been used for this purpose, they are degraded by common impurities of exhaust gases. Therefore, the main challenges for chemical absorption processes are resistance to degradation caused by exhaust gases impurities and the need for a high capacity of regeneration.

Therefore, conventional pulverized fuel systems and circulating fluidized beds are being converted to oxy-combustion, in which O<sub>2</sub> mixed with recirculated flue gases is used instead of air. Thus, a flue gas stream with high concentrations of CO<sub>2</sub> and mainly containing CO<sub>2</sub> and H<sub>2</sub>O is produced, which makes CO<sub>2</sub> separation easier. However, purification of the CO<sub>2</sub> flow to remove incompressible gases is still needed.

Besides this oxy-combustion process (O<sub>2</sub>/CO<sub>2</sub> recycle) followed by post-combustion capture, another option for CCS is pre-combustion capture, in which fuel carbon content is removed before combustion and a CO<sub>2</sub> by-product stream is produced, together with a hydrogen rich fuel. Therefore, coal is first gasified to produce syngas, whose main components are CO and H<sub>2</sub>. Syngas may also be produced from natural gas by steam reforming or partial oxidation. Next, CO is



**Figure 7.5** Different options for CO<sub>2</sub> capture

converted into more H<sub>2</sub> and CO<sub>2</sub> in the presence of steam by water-shift reaction. Therefore, the final CO<sub>2</sub> concentration is much higher, with an easier CO<sub>2</sub> separation process. Different technologies for CO<sub>2</sub> separation are under development, the most promising being pressure swing adsorption (PSA) and membrane or cryogenic separation, as mentioned in Section 7.3.3. These technologies are more attractive for syngas than for exhaust gas, because syngas is cleaner and, due to its higher pressure and high CO<sub>2</sub> content, it is possible to liquefy it by cooling. Afterwards, the produced CO<sub>2</sub> rich stream is going to storage and the H<sub>2</sub>-rich fuel can be used for energy production in a gas turbine combined cycle or in fuel cells to produce electricity.

Gnanapragasam *et al.* [43] studied the effect of gasification operating conditions on reducing CO<sub>2</sub> emissions for an IGCC power generation system. As reported by these authors, the release of CO<sub>2</sub> depends on gasification conditions, namely higher O<sub>2</sub> contents leads to the formation of higher CO<sub>2</sub> amounts, whilst the rise of steam input decreases the release of CO<sub>2</sub>. The type of fuel gasified also affects the formation of CO<sub>2</sub>. Gnanapragasam *et al.* [43] studied four different types of solid fuels including coal and biomass species and verified that the highest CO<sub>2</sub> contents were obtained with wood chips. CO<sub>2</sub> formation is also affected by the temperature conditions of the IGCC unit; to decrease CO<sub>2</sub> it is important not to increase the compressed air temperature prior to its entrance in the gas turbine combustion chamber. The lowest CO<sub>2</sub> emissions were also obtained for a lower inlet temperature in the heat recovery steam generator and a higher gas turbine inlet temperature.

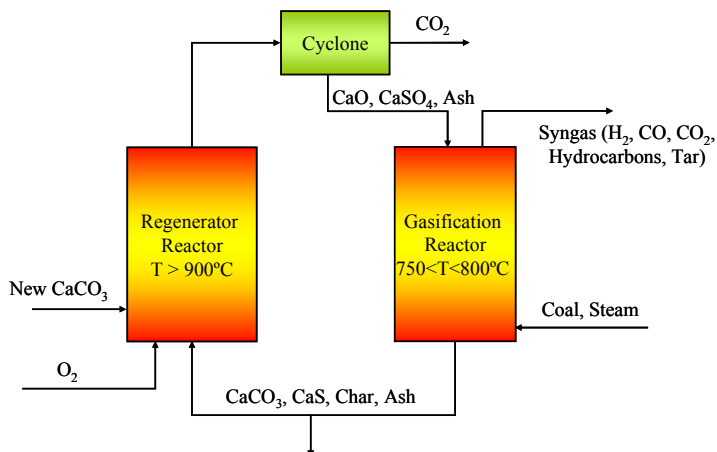
As analyzed in Section 7.3.2, electricity cost is higher when CO<sub>2</sub> capture units are included, because CO<sub>2</sub> removal needs a great deal of energy, thus decreasing process global efficiency. Kanniche *et al.* [44] calculated the cost of electricity production from coal and gas when CO<sub>2</sub> is captured and also the cost of each CO<sub>2</sub> ton captured. These authors studied different options for CO<sub>2</sub> capture: pre-combustion, oxy-combustion and post-combustion. For the first option IGCC was analyzed, considering two gasification types, a conventional process with gasification of dry coal, and with classical combined cycle, producing a gross power output of 320 MWe and a new technology with coal and water slurry gasification integrated in a advanced combined cycle (with steam cooling of the combustion turbine blades), producing a gross power output of 1200 MWe.

For the oxy-combustion option, two types of pulverized coal (PC) power stations were analyzed by Kanniche *et al.* [44]: a sub-critical power station, whose gross power output was 600 MWe and a super-critical power station with a gross power output of 1200 MWe. Two NGCC (Natural Gas Combined Cycle) combined cycles were also studied, one with a 9H type combustion turbine, an evaporation boiler line and a single shaft steam turbine, supplying a gross power of 480 MWe and the other with 9H type combustion turbines, two evaporation boilers and one steam turbine line, which provided 960 MWe. NGCC could be modified to the three capture methods: pre-combustion, oxy-combustion, and post-combustion. In the pre-combustion option, methane was reformed, while CO was converted into CO<sub>2</sub>, which is afterwards captured. According to Kanniche *et al.* [44] this option is more expensive than the others, being only attractive for hydrogen production.

Kanniche *et al.* [44] results showed that the highest efficiency was obtained for NGCC with post-combustion capture (50%), being followed by oxy-combustion in PC (35%), and by IGCC (33.5%), and the lowest efficiency was obtained for post combustion capture in PC (30%). In relation to investment the least expensive technology was NGCC, followed by PC and IGCC with slurry. Oxy-combustion PC and IGCC with slurry led to the lowest production costs. IGCC with slurry, together with oxy-combustion in PC and the current IGCC led to the lowest costs per ton of CO<sub>2</sub> capture. The highest value was obtained for NGCC pre-combustion capture. With the results obtained it was difficult to select the best option for CO<sub>2</sub> capture.

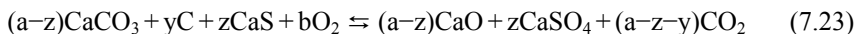
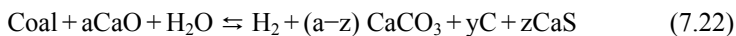
Another method for CO<sub>2</sub> capture is chemical looping (CLC), which consists of two reactors. An oxygen carrier metal is used inside the gasifier which, by being reduced, supplies the oxygen needed for fuel gasification to produce syngas. The reduced metal oxide goes to another reactor, where it is again oxidized in the presence of air. Different metals may be used as oxygen carriers, such as nickel, manganese, calcium, or iron oxides stabilized in a support material like alumina or zirconia. CaO is the most used oxygen carrier, which inside the gasifier is converted into CaCO<sub>3</sub>. The solid produced in the gasifier also contains CaS, char, and ash, which goes into the regenerator, where CaCO<sub>3</sub> is again transformed into CaO, producing a CO<sub>2</sub> stream with high purity ready for storage, as shown in Figure 7.6.

This technology does not need sulfur removal units, water gas shift reactors, or membranes, as all these processes are included in reaction (7.22). Char oxidation



**Figure 7.6** Schematic diagram of conventional chemical looping

in the regeneration reactor supplies some of the heat needed for the regeneration reactor, reaction (7.23). The use of coal with high ash and sulfur content obliges to frequent solids purge:



Rezvani *et al.* [45] analyzed the techno-economic viability of different CO<sub>2</sub> capture technologies, using the simulation software ECLIPSE: physical absorption, water gas shift reactor membranes, and two chemical looping combustion cycles (CLC) with single and double stage reactors.

A water gas shift reactor was used to convert CO into CO<sub>2</sub>, which was removed by physical absorption processes with Selexol solvents and is then compressed to 110 bar for pipeline transportation. The H<sub>2</sub> produced was mixed with N<sub>2</sub> and went into a gas turbine for power generation. The exhaust gases went to a steam generator and next to a steam turbine. In another configuration a water gas shift membrane reactor (WGSMR) and an oxygen transport membrane (OTM) were considered to increase power plant efficiency. OTM was used to recover the remaining gas combustibles in the retentate side of WGSMR.

In the CLC option the gas that left the oxidation reactor went to a gas turbine for power generation and then went through a steam generator to produce steam for a steam turbine for more power generation. The flue gas that left the fuel reactor also went to a gas turbine and next to a steam generator and through the gas condenser prior to the CO<sub>2</sub> compression unit. Because of the exothermic reactions, temperature may reach values that lead to sintering and agglomeration of the oxygen carrier material. To reduce the temperature, the oxygen carrier metal may be cooled down with additional air or, alternatively, by a double stage CLC reactor. In this new configuration, the air that left the oxidation reactor went into a gas

turbine, where both temperature and pressure decreases before it went into the second oxidation reactor. Associated with each oxidation reactor there was a fuel reactor, the flue gases from these two reactors going to the same gas turbine, while there was a separate gas turbine for each exhaust gas coming from the oxidation reactor. The gases leaving each gas turbine were used to produce steam for steam turbines to produce electricity.

Rezvani *et al.* [45] studies showed that the membrane option was a promising one, though the development of hydrogen selective membranes that are more economic and efficient is still needed. The CLC options had high costs, were not able to produce  $H_2$ , and further research is needed before a robust technology is available.

CCS still has many doubts, uncertainties and knowledge gaps, especially concerning life-cycle effects, storage capacity, and permanence and cost. However, these difficulties must not be taken as an excuse for stopping research studies. More technical and engineering data are still needed since not all the technologies analyzed are at the same stage of development and deployment and some of them still need further demonstration on a larger scale. On the other hand, economic estimations are dependent on fuels and other materials supply restrictions, and on equipment costs, which may suffer alterations depending on the maturity of technologies and on the amount of equipment produced. Therefore more evaluation studies are still needed for accurate technical, economic, and environmental estimations.

Though  $CO_2$  capture is expensive and more fuel is spent to produce the same amount of electricity, effective CCS is fundamental for sustainable development, to prevent climate change, and to guarantee that life on planet Earth will continue as we know it. To achieve these goals and to accomplish zero emissions, biomass and wastes gasification will probably have an important role. The success of CCS also depends on strong policy framework, and governments of all nations, especially those from G8, have an important role in establishing sufficient and long-term incentives for CCS and for building  $CO_2$  transportation networks.

## 7.5 Main Gasification Barriers and R&D Needs

Through gasification technologies it is possible to produce heat, power, CHP (combined heat and power), and synthesis gas. However, the main challenge for gasification technologies is the accomplishment of higher efficiency energy conversion, low environmental impact, and low cost in order to ensure sustainable development. It is desirable that gasification plays an important role in energy production in the near future, as it permits an easier  $CO_2$  separation than other technologies. However, there are still some barriers that gasification needs to overcome:

- flexibility of gasification systems to diversify the type of feedstock: fossil fuels, different types of biomass and wastes or blends of both;
- efficient syngas cleaning processes;
- high efficiency of integrated gasification combined cycle (IGCC);

- development of efficient syngas chemical synthesis;
- process scale-up and fabrication;
- process demonstration at commercial scale;
- sustainable policies.

Gasification of low grade coals and of different types of wastes with high contents of undesirable elements may lead to the release of pollutants precursors into the syngas. Some of these feedstocks may also be more difficult to gasify, thus requiring more severe gasification conditions, new materials and/or coatings for existing materials, and the use of more expensive catalysts or sorbents to guarantee syngas quality. One of the key issues for gasification technologies spread is the development of effective gas cleaning processes to ensure the production of high quality syngas even when poor or low quality feedstocks are gasified. Research and development of low cost and efficient catalysts is most needed to achieve effective abatement of undesirable syngas components, like tar, S, N, and halogens compounds. Catalyst regeneration and the development of multi-function catalysts for simultaneously reducing different types of compounds, thus eliminating some steps of syngas cleaning treatments, are important issues. Technical, economical, and environmental viability improvements of the overall process are dependent on new catalysts development.

The success of liquid fuels production from syngas through chemical synthesis is also dependent on advances on more selective catalysts, for the production of specific compounds, thus allowing the simplification of products separation processes and the improvement of technical and economical viability of the chemical synthesis process. The key issue in pre-combustion technologies for CCS is CO<sub>2</sub> separation, mainly for economic reasons; thus further R&D is still needed to raise process efficiency and decrease materials costs, such as high performance membranes. Long term testing on a commercial scale of new technologies such as IGCC, chemical synthesis and CCS is fundamental to guarantee reliable operation and to validate these processes. On the other hand, as IGCC, chemical synthesis, and CCS installations spread, equipment and materials will be produced on a larger scale, which will decrease production costs.

All the R&D and demonstration activities still need political and funding support through research financing programs, adequate incentives, policies, and strategies. Without public commitment and governmental support CCS and energy production through zero emission technologies will not be accomplished and life on Earth will be put at serious risk.

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